

MODELING OF REACTIVITY OF LEWIS AND BRØNSTED SITES

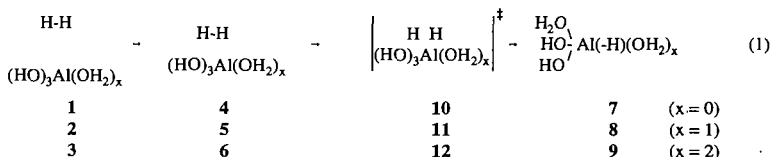
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It is generally considered that the coordinatively unsaturated sites (cus) responsible for the catalytic properties of active aluminum oxide consists of tri- and pentacoordinated aluminum atoms. The remaining possibilities, hexa- and tetraordinated aluminum atoms, are considered coordinatively saturated and, therefore, unreactive. A careful NMR investigation has evidenced, however, only tetra-, penta-, and hexacoordinated aluminum atoms in alumina and in the intracavity material of steamed zeolites. No measurable amount of tricoordinated sites was found.¹ Even if vanishingly small concentrations of tricoordinated aluminum are present, it is difficult to assign all catalytic activity to them. An examination of the relative reactivity of various sites on alumina was, therefore, in order.

The isotope exchange between D₂ and the protons of the solid is a good model reaction for the reactivity of sites on alumina.² Theoretical modeling of the hydrogen chemisorption on alumina was attempted before by both semiempirical³ and ab initio calculations,⁴ at a rather low level of theory. One study considered only tricoordinated sites,^{4a} the other looked at pentacoordinated sites as well and concluded that they were inactive.^{4b} The aluminum sites were modeled by the simple clusters Al(OH)₃ and Al(OH)₅.⁴ It was not clear from the paper^{4b} whether the species considered was the dianion Al(OH)₅²⁻ or a dioxidized, electrically neutral, species of the same formula, but neither of them appears to us to be a good choice.

We considered the reactivity of electrically neutral single clusters, (HO)₃Al(OH₂)_x, containing tri- (1, x = 0), tetra- (2, x = 1), and pentacoordinated (3, x = 2) aluminum atoms. Thus, no unnatural, oxidized species was used. The full reaction profile for dissociative hydrogen chemisorption was studied (Eq. 1).



As the first step, the physisorbed complexes 4 (x = 0), 5 (x = 1) and 6 (x = 2) were examined. Their reaction to form the chemisorbed complexes, 7, 8, and 9, was mapped to determine the transition structures (10, 11, and 12) and the corresponding energies (E_{TS}), which measure the energy barriers for the exchange.

The ab initio calculations were conducted with the program Gaussian 94,⁵ in the manner described previously.⁶ All geometry optimizations were conducted with electron correlation with the MP2 method⁷ or with the DFT-B3LYP⁸ method. The 6-31G*, 6-31-G**, 6-31++G**, 6-311G** and 6-311++G** basis sets were used.

For the tricoordinated aluminum system (x = 0), the geometry of the starting cluster was obtained by the optimization of the species (HO)₃Al(OH₂) (2) and removal of the extra water molecule, on the idea that aluminum oxide surfaces are formed by calcination of hydrated forms. In one approach (A), the angles around the aluminum atom were then frozen as in the hydrated cluster and the other geometrical parameters of the dehydrated cluster were optimized. Alternatively (B), the rigidity of the solid was simulated by freezing the hydrogen atoms in their positions in the hydrated cluster and then optimizing the central part of the cluster (the Al(-O-)₃ group) after the removal of the extra water. The complexes with physisorbed and chemisorbed hydrogen were optimized in the same way. The reactions of tetra- and pentacoordinated aluminum clusters were studied without any constraints on the geometry.

The calculations predicted the hydrogen chemisorption to be endothermic in all cases, the order being $E(x=0) < E(x=1) < E(x=2)$. For $x=0$, the calculation by the approach B gave a much lower endothermicity for the chemisorption than the approach A. The energy barriers for chemisorption were similar, however, for the approaches A and B. Their variation with the coordination number of the aluminum atom was $E_{TS}(x=0) < E_{TS}(x=1) < E_{TS}(x=2)$. Reaction coordinate tracking indicated that chemisorption occurs through the interaction of H_2 with the Al atom, therefore it is a catalysis by a metal ion. A three-center bond involving the aluminum and the two hydrogens is formed, after which one of the hydrogens migrates to an adjacent oxygen atom. the transition state is located along this hydrogen shift.. B3LYP calculations give results in reasonable agreement with the MP2 calculations, attesting to the appropriateness of the DFT method for this type of structures.

The calculations indicate tetracoordinated aluminum sites to be catalytically active. As these sites are usually in higher concentration than the pentacoordinated sites and are intrinsically much more active, they should be considered *the* catalytic sites on active alumina.

The second type of acid sites on solid surfaces, the Brønsted sites, are most often characterized by neutralization with a probe base and examination of the product by spectroscopic methods or measurement of the thermal effect of this interaction.⁹ Pyridine (Py) and its derivatives have long been used as probe bases. Comparison of pyridine with 2,6-disubstituted pyridines was proposed to distinguish Lewis from Brønsted sites.¹⁰ The application of the highly crowded homolog, 2,6-di-*tert*-butylpyridine (DTBP) was proposed to distinguish between sites on the outer surface and sites inside cavities or channels.¹¹

It has been pointed out that all types of ionic reactions on solid surfaces must occur through the intermediacy of tight ion pairs.^{9a,12} Thus, the reaction of Py forms PyH^+A^- tight ion pairs, where A^- is the anion of the acid site. The direction of adsorption should be the one which maximizes the hydrogen bonding interaction, that is with the N^+-H perpendicular to the surface (sideways adsorption). A complete analysis of the thermodynamics of protonation in the gas phase and in water solution led to the conclusion that $DTBP^+A^-$ also forms hydrogen bonds at nitrogen.¹³

The line-shape of the NMR signals of protons bonded to nitrogen in pyridinium (PyH^+) and di-*tert*-butylpyridinium ions ($DTBP^+$) in solution indicated a significant difference in their rates of longitudinal relaxation (R_1), the former ion relaxing the slowest. Computer modeling showed that the ratio of relaxation rates is 10-20. A significant difference between the relaxation times ($T_1 = 1/R_1$) for the carbon atoms in β and γ position (4.71 and 4.75 sec for PyH^+ , 0.55 and 0.79 sec for $DTBP^+$) was observed as well. The different positions in the molecule of the N-H group and of those two carbon atoms indicate that the difference in longitudinal relaxation rates originates in a different rate of tumbling in solution, rather than a difference in the electrical field gradient. Calculations of the correlation times for the relaxation of molecules considered as ellipsoid-shape rotors in a medium of given viscosity indicate that the difference in size covers only a part of the difference in tumbling rates (lower τ_c for pyridine). The difference should come from specific interactions with the solvent, most likely in the form of electrical double layers which have to be disturbed during the rotation.

Differences between relaxation times for each individual ion in different acids were also observed. It was established that the differences are not solvent effects, but are brought about by the change in anion. Thus, in the same solvent PyH^+ relaxes slower, that is, tumbles faster, when the anion corresponds to a stronger acid. The reason for this behavior is that in the salt of the weaker acid the ions are ion-paired and the rotation, occurring around an axis perpendicular to the $N-H^+$ bond, is hindered by this interaction.

The opposite effect is observed for the $DTBP^+$ cation: the salt of the *weaker* acid, which is present in solution as ion pairs, tumbles faster (relaxes more slowly). This behavior can be rationalized by the anion being situated in the ion pair along the axis around which the molecule rotates to produce the NMR relaxation, that means, at the top of the ring. Therefore, no hydrogen bond $N-H^+ \cdots A^-$ is formed for this cation, a finding which contradicts the assertions of previous authors.¹³

The same orientation should be encountered in chemisorption of DTBP on solid acids, that is with the ring facing the solid surface containing the acid site.

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